

# PATENT SPECIFICATION

DRAWINGS ATTACHED

1,043,082

1,043,082



Date of Application and filing Complete Specification: Jan. 8, 1964.  
No. 819/64.

Application made in Germany (No. C28868 IVd/39c) on Jan. 9, 1963.

Complete Specification Published: Sept. 21, 1966.

© Crown Copyright 1966.

**Index at acceptance:**—C3 P(7C12B, 7C17, 7C18, 7C20B, 7C20D1, 7C20D3, 7D1A, 7D1C, 7D1X, 7D2A1, 7FX, 7K7, 7T2B)

**Int. Cl.:**—C 08 f 27/26

## COMPLETE SPECIFICATION

### A method of Controllably Thermally Degrading Thermoplastics

We, CHEMISCHE WERKE HÜLS AKTIENGESELLSCHAFT, a German Company, of 4370 Marl, Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

It is known that high molecular weight substances can be structurally changed by the expenditure of mechanical or thermal energy, the result being for instance depolymerisation, the formation of cross links or gelation. Whereas in the processing of natural or synthetic rubber a preceding process of mastication may be performed to facilitate processing, product decomposition is most undesirable for instance when injection moulding a plastic.

For the production of thin section shapes, such as polyolefine foils or flasks, lower molecular weight polyolefines are required which are very difficult to provide because such polymers are frequently spoilt by exhibiting spatters and contaminations. Repeated attempts have therefore been made controllably to degrade the more easily produced higher molecular weight thermoplastics with a view to obtaining satisfactory polymers of lower molecular weight.

For instance, it has been proposed to treat solutions of polypropylene in an inert hydrocarbon in the presence of steam and air or oxygen-supplying compounds at temperatures between 70° and 240°C, particularly between 150° and 200°C. Although these processes do lead to uniformly degraded products, the quantity of solvents required and the reaction space necessitated by the low reaction speeds and the low concentrations in the solvent of the polymer that is to be degraded exceed economically acceptable limits for large scale industrial production.

Another known method comprises degrading polypropylene at temperatures between 250° and 350°C or in the presence of oxygen at temperatures between 150° and 180°C. However, in this method considerable difficulties

are likewise encountered. On the one hand, the treatment of polypropylene at temperatures between 250° and 350°C facilitates cracking reactions which badly contaminate the final product and power consumption is also extremely high. On the other hand, thermal treatments with oxygen are difficult to perform because a completely uniform distribution of the oxygen is impossible to achieve.

We have now found that thermoplastics can be controllably and uniformly degraded and the above mentioned difficulties readily overcome by intimately commixing the powdered, cold compacted, sintered or molten thermoplastics with free-radical-forming compounds in quantities between 0.001 and 10%, particularly between 0.005 and 0.1% by weight, related to the thermoplastic and by treating the pulverulent, cold compacted, sintered or molten mixture above the decomposition temperature of the free-radical-forming compounds.

Degradation is advantageously performed at temperatures between 60° and 300°C, preferably below 150°C. From the economic point of view it is desirable that the degradation temperature be as low as possible.

This method permits thermoplastics like polyolefines, such as polyethylene, polypropylene, polybutylene, polystyrene, and copolymers of ethylene and propylene, ethylene and butylene, propylene and butylene, preferably having reduced viscosities between 2 and 10, to be reproducibly and controllably degraded to polymers having reduced viscosities between 1 and 4, particularly between 1.5 and 3.0. Suitable free-radical-forming compounds include peroxides, azo-compounds, per-acids and their salts, preferably compounds such as di-tert.-butyl peroxide, lauryl peroxide, potassium persulphate and azodiisobutyric dinitrile, which have decomposition temperatures below 200°C. Compounds such as benzoyl oxide permit degradation to proceed in a particularly gentle manner at temperatures which are as

50

55

60

65

70

75

80

85

90

low as 60° to 120°C. It is advisable to select these compounds in such a way that their processing temperatures only slightly exceed their decomposition temperatures. For further reducing the temperatures of degradation a useful step consists in adding catalysts, such as heavy metal compounds, for instance ferrous sulphate, to the radical-forming compounds. Suitable stabilisers which may be added if desired are phenolic antioxidants, sulphur- or nitrogen-containing compounds, such as 2,6-di-tert.-butyl-4-methylphenol, N-stearoyl-p-aminophenol or diamine, in quantities between 0.01% and 1.0%. These stabilisers as well as the radical-forming compounds may be added in the form of solids, suspensions or solutions. Moreover, the thermoplastic in question may contain conventional additives, such as plasticisers, extenders, fillers and lubricants.

The degree and rate of degradation primarily depend upon the quantity and nature of the radical-forming compounds and upon the temperatures used. In a first approximation the quantity and proportion of free radicals present at the prevailing temperature as well as the nature of the radical-forming compounds determine the degree of degradation, whereas the rate of degradation is controlled by the temperature. It has been found that it is immaterial when performing the proposed method whether the radical-forming compounds are introduced in the form of liquids or solids in pure form or in solution, emulsion or dispersion. Furthermore, the particular instant at which prior to the beginning of the reaction the addition is made makes no difference. It is also possible to degrade polymers which have already been stabilised. Nevertheless, the stabiliser need not be added until degradation has taken place. Moreover, the process of degradation can be interrupted by abrupt cooling and it may then be continued again by subsequently raising the temperature and carrying out further processing of the thermoplastic, for example in an injection-moulding machine. Degradation is not affected by the presence in the polymer that is to be degraded of some remaining inert solvent up to about 5% related to the polymer. This can be removed before or during the reaction, say in a vacuum. Degradation can be performed either in the molten or in the pulverulent or sintered state. On the other hand, atmospheric oxygen is a factor which interferes with the reproducibility of the reaction because the volume of air which is actively present cannot be readily ascertained. It is therefore advisable to perform the reaction substantially in the absence of air, for instance in an inert gas such as nitrogen, argon or in solvent vapours.

By observing the above-described optimum conditions the process may preferably be performed in an extruder. Despite the short periods of residence which are in practice available, the considerable magnitude of the shearing forces permits the polymer which is to be degraded to be easily and very quickly raised to the necessary temperature and then cooled immediately degradation has taken place.

The described method therefore allows the degradation reaction which proceeds at a very high rate to be reliably controlled.

The proposed method will now be particularly described by reference to a preferred way of carrying the same into effect. It will be understood from the accompanying drawing that the screw shaft 1 of the extruder carries the following types of screw thread which may be machined into the shaft or mounted thereon in the form of threaded sleeves:—

- (a) A high pitch feed section 2
- (b) A low pitch compressing section 3
- (c) A back-pressure generating section 4, and
- (d) A high pitched degasification and ejection section 5.

The thermoplastic which is to be degraded is loaded into the extruder through a charging opening 6, entrained by the feed section 2 and conveyed into the extruder casing 7. The radical-forming compound is introduced through a second charging opening 8. The two substances are conveyed into the compressing section 3 where they are intimately mixed and raised to reaction temperature by the kneading and mixing action of the extruder as well as by heat applied from the outside. The polymer may be in the state of a melt, a powder or sinter. When degradation has been completed the stabiliser is added through a charging opening 9 and then protects the polymer against further change. The back-pressure generating discs 4 give rise to the formation of a plug of material which separates the reaction chamber 10 from the degasification chamber 11. In the latter chamber 11 residual quantities of solvent are removed from the polymer, possibly under vacuum, and the polymer is then forced through the dieplate 12 and extruded in the form of a section of any required shape which may then be cut up into granulates.

This process may be modified in appropriate manner in several ways. For instance, the polymer which is to be degraded may be processed in the form of a dry or moist powder or of a suspension. In the latter case the solid is separated from the major part of the solvent before the radical-forming compound is added. The latter as well as the stabiliser may be directly added to the polymer that is to be degraded, either together or separately.

Apart from single or multiple-screw extruders suitable apparatus for performing the method include kneaders, melting pots or sinter mixers. The method can be performed either in continuous or batchwise operation.

The invention is further illustrated by the

available, the considerable magnitude of the shearing forces permits the polymer which is to be degraded to be easily and very quickly raised to the necessary temperature and then cooled immediately degradation has taken place.

The described method therefore allows the degradation reaction which proceeds at a very high rate to be reliably controlled.

The proposed method will now be particularly described by reference to a preferred way of carrying the same into effect. It will be understood from the accompanying drawing that the screw shaft 1 of the extruder carries the following types of screw thread which may be machined into the shaft or mounted thereon in the form of threaded sleeves:—

- (a) A high pitch feed section 2
- (b) A low pitch compressing section 3
- (c) A back-pressure generating section 4, and
- (d) A high pitched degasification and ejection section 5.

The thermoplastic which is to be degraded is loaded into the extruder through a charging opening 6, entrained by the feed section 2 and conveyed into the extruder casing 7. The radical-forming compound is introduced through a second charging opening 8. The two substances are conveyed into the compressing section 3 where they are intimately mixed and raised to reaction temperature by the kneading and mixing action of the extruder as well as by heat applied from the outside. The polymer may be in the state of a melt, a powder or sinter. When degradation has been completed the stabiliser is added through a charging opening 9 and then protects the polymer against further change. The back-pressure generating discs 4 give rise to the formation of a plug of material which separates the reaction chamber 10 from the degasification chamber 11. In the latter chamber 11 residual quantities of solvent are removed from the polymer, possibly under vacuum, and the polymer is then forced through the dieplate 12 and extruded in the form of a section of any required shape which may then be cut up into granulates.

This process may be modified in appropriate manner in several ways. For instance, the polymer which is to be degraded may be processed in the form of a dry or moist powder or of a suspension. In the latter case the solid is separated from the major part of the solvent before the radical-forming compound is added. The latter as well as the stabiliser may be directly added to the polymer that is to be degraded, either together or separately.

Apart from single or multiple-screw extruders suitable apparatus for performing the method include kneaders, melting pots or sinter mixers. The method can be performed either in continuous or batchwise operation.

The invention is further illustrated by the

1,043,082 COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of  
the Original on a reduced scale.*

